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Synthesis and characterization of aluminum or copper tungstophosphate and tungstosilicate immobilized in a polymeric blend

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Abstract

Aluminum or copper tungstophosphates and tungstosilicates were synthesized and immobilized in a polymeric blend formed by polyvinyl alcohol and polyethylene glycol using the freeze-thawing method. The salts retained the Keggin structure of the heteropolyanions during their synthesis and immobilization. Materials with spherical shape and a mean size of 2 mm were obtained, with an almost constant distribution of the salts along the sphere width. Besides, the immobilized salts presented very strong acid sites and good thermal stability. The synthesized hybrid materials present suitable properties to be used as heterogeneous acid catalysts which are very attractive for many processes as replacement of conventional liquid ones.

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1. Introduction

The strong acidity of heteropolyacids (HPA) and some of their salts [1–3] make them suitable as catalysts for many acid-catalyzed reactions. Since they are less corrosive and produce lower amount of waste than conventional acid catalysts, they can be utilized as replacement in environmentally benign processes.

The use of a support allowing the HPA to be dispersed over a large surface may result in an increase of its catalytic activity. The properties as well as the catalytic behavior of supported HPA catalysts depends on the carrier, the HPA loading, conditions of pretreatment, among other variables. Diverse supports have been tested, acidic or neutral solids such as active carbon, SiO_2 and ZrO_2 being suitable as carriers [4]. But HPA often leaks out of catalyst supports even in vapor-phase reactions. It is important, for practical purposes, to develop supported catalysts which can be applied to several reactions without HPA leakage.

With regard to the salts of the heteropolyacids, the cation type, the constituent elements of the polyanion and the tertiary structure influence on their

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properties. The partial hydrolysis and the presence of inhomogeneities resulting from the synthesis also have an influence. Two groups of the salts of the Keggin HPA are mentioned in the literature [1]. The salts of large cations (classified as type B) are insoluble in water, have high specific surface area and relatively high thermal stability. The salts of small cations (classified as type A) are very soluble in water or polar organic solvents, posses a low specific surface area, and in general behave in many respects in a similar way to the parent acid. A support that firmly immobilizes the type A salts will make it possible to carry out reactions in liquid phase, using the obtained materials as catalysts that can be easily separated from the reaction medium.

A new type of supports can be obtained using polymers as starting materials. They can be used when the catalysts are employed in reactions carried out at relatively low temperatures, due to their instability at high temperature. In the field of biotechnology, polyvinyl alcohol has been used to encapsulate enzymes or cells. Recently, the immobilization of *Lactobacillus kefir* in polyvinyl alcohol for the synthesis of hydrophobic quiral alcohols in organic solvents has been studied [5]. A disadvantage is that polyvinyl alcohol tends to be dissolved in water when it is not cross-linked. However, it has been reported that PVA has good ability to form hydrogels by chemical cross-linking with boric acid or formaldehyde [6]. In the field of electrocatalysis, the use of polypyrrole, polytiophene, and polyaniline as heteropolyanion supports has been reported [7].

The polymer-immobilization of heteropolycompounds with Keggin structure is scarcely presented in the literature. Films of polyvinyl alcohol together with molybdotungstovanadogermanic acid have been prepared, and their conductivity properties have been studied [8]. Hasik et al. [9] have reported the catalytic performance of tungstophosphoric acid supported on polyaniline in the reaction of isopropanol decomposition. They have also found that an HPA molecular dispersion is reached through a protonation reaction. On the other hand, HPA-polymer composite materials have been prepared, using molybdophosphoric acid, and polyphenylene oxide, polyethersulfone, and polysulfone [10]. They showed a higher catalytic activity than the bulk acid in the synthesis of *tert*-butanol in liquid phase. Besides, the molybdophosphoric acid, entrapped in polyvinyl alcohol cross-linked with succinic acid,

has been utilized as catalyst in the dehydration of α-pinene to obtain α-terpineol [11].

Aluminum or copper tungstophosphate and tungstosilicate can present interesting characteristics as catalysts since they can have Lewis and/or Brønsted acidity, their immobilization in polymeric materials being an original subject. The aim of the present work is to make a contribution to the knowledge of the properties of polymer-immobilized heteropolycompounds through the synthesis and characterization of these salts immobilized in a physical cross-linked blend constituted by polyvinyl alcohol (PVA) and polyethylene glycol (PEG), and to study their acidic characteristics.

2. Experimental

2.1. Salt synthesis

The aluminum or copper salts of the tungstosilicic (TSA) and tungstophosphoric (TPA) acids, named AlTSA or CuTSA, and AlTPA or CuTPA, respectively, were prepared from aqueous solutions of the corresponding acids ($H_4SiW_{12}O_{40} \cdot 23H_2O$ and $H_3PW_{12}O_{40} \cdot 21H_2O$, Fluka p.a.), to which the required stoichiometric amount of the cation was added [12,13], employing $Cu[NO_3]_2$ or $Al_2[SO_4]_3$ (Merck p.a.) as cation source. The resulting solution was stirred at room temperature for 60 min, and then evaporated till dryness in air at 70 °C. The salts were recrystallized, washed with ethanol, and dried again at 70 °C.

2.2. Salt immobilization

The synthesized salts were immobilized in PVA-PEG gel beads (mean diameter: 2 mm) prepared using the freezing-thawing method [14]. The polymer solution was prepared by solving PVA (Mallinckrodt, 2.2 g) in a hot mixture of PEG (Mallinckrodt, 2.0 g) and water (18 g). After that, an aqueous solution of the salts was added under vigorous stirring. The resulting solution was slowly dropped into liquid nitrogen. After freezing, the beads were slowly thawed after nitrogen was evaporated, using a Dewar vessel. The amount of salt was fixed in order to obtain a concentration of 30% by weight in the final material. The obtained polymer-immobilized aluminum (AlTSA$_{PVA-PEG}$ and AlTPA$_{PVA-PEG}$) and copper (CuTSA$_{PVA-PEG}$ and CuTPA$_{PVA-PEG}$) salts were dried at 110 °C.

In order to evaluate the good ability of PVA-PEG to immobilize the tungstophosphates and tungstosilicates salts, Al(Cu)TPA$_{PVA-PEG}$ and Al(Cu)TSA$_{PVA-PEG}$ samples were refluxed in toluene or dichloromethane using a Soxhlet apparatus for 2 h.

2.3. Physicochemical characterization

The specific surface area of the salts was estimated by the BET method from the adsorption–desorption isotherms of nitrogen at $-196\,°C$, using ASAP 2020 Micromeritics equipment, with the samples previously degassed at $100\,°C$ for 1 h.

The X-ray diffraction patterns (XRD) of the bulk and immobilized salts were obtained with PW-1417 Philips equipment, using Cu Kα radiation, Ni filter, 20 mA and 40 kV in the high voltage source, a scanning angle between $5°$ and $60°$ 2θ, and a scanning rate of $1°$ per minute.

A Philips 505 scanning electron microscope was employed to obtain micrographs of the PVA-PEG-immobilized salts. The radial distribution of the salts in the spheres was determined using an energy dispersive X-ray analysis system (EDAX).

To obtain the Fourier transform infrared (FT-IR) spectra, IFS 66 Bruker equipment and pellets of the samples in KBr were utilized. The measurements were performed in the range 400–1500 cm^{-1}.

The thermogravimetric analysis (TGA) and the differential scanning calorimetric (DSC) study were carried out using DT 50 Shimadzu equipment, in argon or nitrogen atmosphere, sample weight 25–50 mg, and heating rate $10\,°C$ per minute.

For the potentiometric titration, 0.05 g of solid were suspended in acetonitrile (90 ml) and stirred for 3 h. The suspension was titrated with a 0.05 N solution of n-butylamine in acetonitrile. The potential variation was measured with a Hanna 211 pH meter and a double junction electrode.

3. Results and discussion

The copper or aluminum tungstosilicate and tungstophosphate, synthesized employing Cu[NO$_3$]$_2$ or Al$_2$[SO$_4$]$_3$ presented a specific surface area calculated by the BET method, lower than 10 m^2/g. The low specific surface area of Cu(Al)TSA and Cu(Al)TPA samples are characteristic of Type A salts [13].

The FT-IR spectra of the AlTPA and CuTPA salts dried at $70\,°C$ present the characteristic bands of the $[PW_{12}O_{40}]^{3-}$ anion. These bands, from the FT-IR spectrum of TPA dried at $70\,°C$, are placed at 1081, 982, 888, 793, 595, and 524 cm^{-1}, in accordance with those reported in the literature for the $H_3PW_{12}O_{40}$ acid [15]. The first five bands are assigned to the P–Oa, W–Od, W–Ob–W, W–Oc–W stretchings, and to Oa–P–Oa deformation, respectively. The subscripts correspond to oxygens binding W and P (a), or bridging different WO$_6$ octahedra that share corners (b) or edges (c), and terminal oxygens (d) bonded to only one W atom. However, in the salts, the band assigned to the W–Od stretching is broadened, as a result of the splitting into two components. The new component may be a result of the interaction between the $[PW_{12}O_{40}]^{3-}$ anion and the Al^{3+} or Cu^{2+} cations.

Bands at 1019, 982, 926, 884, 778, and 541 cm^{-1} are present in the FT-IR spectrum of bulk TSA, which coincide with those referred to in literature [15] for this heteropolyacid. The same bands are observed in the spectrum of the AlTSA salt dried at $70\,°C$ (Fig. 1a), although the band placed at 982 cm^{-1} (stretching of the W–Od terminal bond) has a slight broadening, and a shoulder at 999 cm^{-1}. In addition, the band at 884 cm^{-1} (W–O–W bridged bond) shows a shoulder at 892 cm^{-1}. These effects can appear as a result of the interaction between the $[SiW_{12}O_{40}]^{4-}$ anion and the Al^{3+} cations. A similar behavior was found for the CuTSA salt.

During the synthesis of the salts, the partial transformation of $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$ anions into the $[PW_{11}O_{39}]^{7-}$ and $[SiW_{11}O_{39}]^{8-}$ lacu-
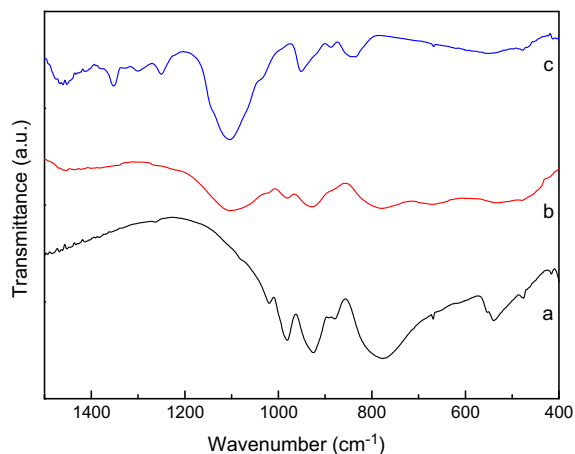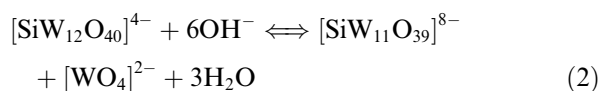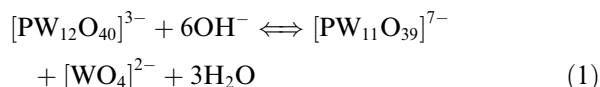

Fig. 1. FT-IR spectra of AlTSA (a) AlTSA$_{PVA-PEG}$ (b), and PVA-PEG (c) samples.

nar phases could take place through the following reactions:

$$[PW_{12}O_{40}]^{3-} + 6OH^- \Longleftrightarrow [PW_{11}O_{39}]^{7-}$$
$$+ [WO_4]^{2-} + 3H_2O \tag{1}$$

$$[SiW_{12}O_{40}]^{4-} + 6OH^- \Longleftrightarrow [SiW_{11}O_{39}]^{8-}$$
$$+ [WO_4]^{2-} + 3H_2O \tag{2}$$

However, neither $[PW_{11}O_{39}]^{7-}$ nor $[SiW_{11}O_{39}]^{8-}$ characteristic bands were present in the FT-IR spectra of aluminum and copper salts of tungstophosphoric or tungstosilicic acid.

For the immobilized AlTSA$_{PVA-PEG}$ (Fig. 1b) and AlTPA$_{PVA-PEG}$ salts, the FT-IR spectra showed the characteristic bands of the $[SiW_{12}O_{40}]^{4-}$ and $[PW_{12}O_{40}]^{3-}$ anions, respectively, overlapped to those of the support (Fig. 1c). The same behavior was found for the CuTSA$_{PVA-PEG}$ and CuTPA$_{PVA-PEG}$ samples.

By this technique it is possible to establish that undegraded Keggin anions are present when the aluminum and copper tungstophosphate or tungstosilicate are immobilized in PVA-PEG, without the presence of the $[PW_{11}O_{39}]^{7-}$ or $[SiW_{11}O_{39}]^{8-}$ lacunar phases.

The freeze-thawing method allowed us to obtain spheres of PVA-PEG blend with a 2 mm mean size, in which the tungstophosphate or tungstosilicate salts are included. The micrographs (Fig. 2) presented a sponge-like structure conformed by a network of cross-linked channels. The microanalysis performed by EDAX, showed that tungsten, aluminum and copper content along the diameter of the spheres is almost practically uniform.

The XRD patterns of AlTSA and CuTSA salts (Fig. 3a and b, respectively) were almost alike, though the copper one was less well crystallized. The lines corresponding to the parent acid $H_4SiW_{12}O_{40} \cdot 23H_2O$ were not present, nevertheless the patterns exhibited lines similar to those of $H_4SiW_{12}O_{40} \cdot 6H_2O$ (Fig. 3c), though slightly shifted. The behaviour resembles what has been reported in the literature for the Na^+ and K^+ type A salts [16].

For the immobilized AlTSA$_{PVA-PEG}$ and CuTSA$_{PVA-PEG}$ samples, XRD patterns similar to that recorded for the spheres prepared from only PVA-PEG blend (Fig. 3d) were obtained. They do not present any of the diffraction lines of the aluminum or copper tungstosilicate, which may be a result of a high dispersion in the polymeric matrix. An entirely alike behaviour was displayed by the AlTPA$_{PVA-PEG}$ and CuTPA$_{PVA-PEG}$ samples.

The DSC diagrams of the aluminum or copper tungstosilicates (Fig. 4) showed several endothermic peaks below 250 °C, and an exothermic peak with a maximum at 549 and 536 °C, respectively. The endothermic peaks are assigned to the removal of physisorbed or crystallization water molecules, whereas the exothermic peak is due to the decomposition of the $[SiW_{12}O_{40}]^{4-}$ anion. It must be noted that the DSC diagrams of AlTPA and CuTPA salts (Fig. 5) showed features similar to those observed for the respective TSA salts. However, the exothermic peak appeared at a slightly higher temperature (603 and 563 °C, respectively) as a result of the higher thermal stability of TPA [1].

On the other hand, the DSC diagram of the PVA-PEG blend (Fig. 6a) used to immobilize the
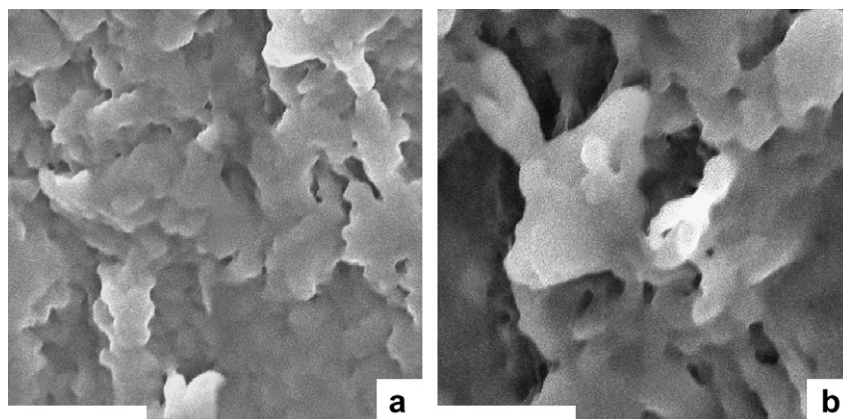

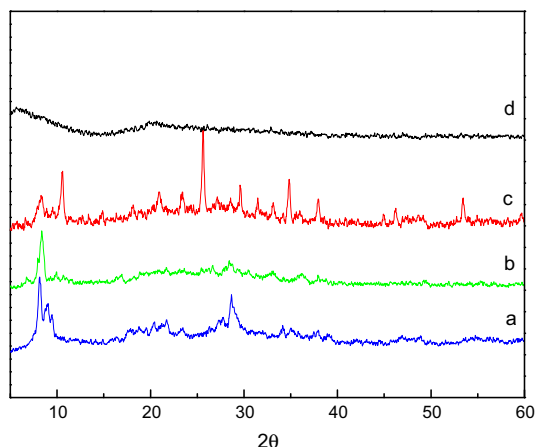Fig. 2. Secondary electron micrograph of AlTSA$_{PVA-PEG}$ sample, bar size 20 μm (a) and (b) 10 μm.

Fig. 3. XRD patterns of AlTSA (a), CuTSA (b), $H_4SiW_{12}O_{40} \cdot 6H_2O$ (c), and PVA-PEG (d) samples.
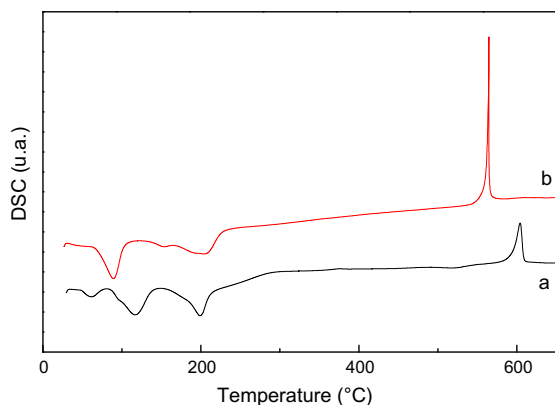

Fig. 4. DSC diagram of AlTSA (a) and CuTSA (b) samples.
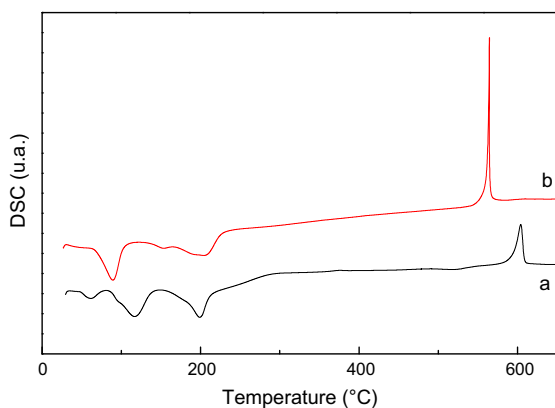

Fig. 5. DSC diagram of AlTPA (a) and CuTPA (b) samples.

salts presented four endothermic peaks at 51, 222, 330, and 444 °C. The first two peaks are associated with the loss of water and other volatile compounds (aldehydes, ketones, and ethers), while those placed
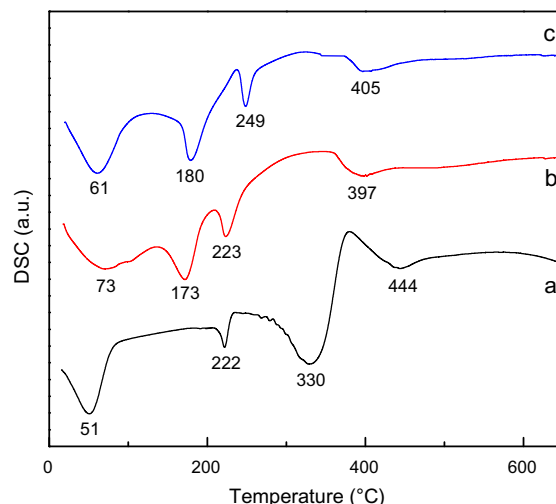

Fig. 6. DSC diagram of PVA-PEG (a), AlTPA$_{PVA-PEG}$ (b), and CuTPA$_{PVA-PEG}$ (c) samples.

above 240 °C are assigned to the removal of alkanes, alkenes, and other unsaturated hydrocarbons, resulting from the thermal degradation of PVA and PEG [17]. The amount of physisorbed water was estimated from TGA in about 11% of the total weight of the PVA-PEG matrix. The matrix is almost completely degraded at temperatures near 500 °C (weight loss higher than 95%).

The immobilized aluminum or copper tungstophosphates (AlTPA$_{PVA-PEG}$, and CuTPA$_{PVA-PEG}$) showed, in the DSC diagrams (Fig. 6b and c), the endothermic peaks associated with the elimination of aldehydes, ketones, ethers, and other saturated and unsaturated hydrocarbons shifted to lower temperatures. The exothermic peak assigned to $[PW_{12}O_{40}]^{3-}$ anion decomposition does not appear in the temperature range studied, unless it is masked by the decomposition of the polymeric support. The same behavior was found for the immobilized aluminum or copper tungstosilicates (AlTSA$_{PVA-PEG}$ and CuTSA$_{PVA-PEG}$).

The titration with n-butylamine allows us to estimate the strength and the number of acid sites present in the salts. The initial electrode potential (E_i) indicates the maximum strength of the acid sites and the value from which the plateau is obtained (mequiv. amine/g salt) could be used to carry out a comparison of total number of acid sites of different samples. The strength of the acid sites can be classified according to the following scale: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 < E_i < 0$ mV (weak sites), and $E_i < -100$ mV (very weak sites) [18].

The potentiometric titration curves of the immobilized salts showed that the AlTPA$_{PVA-PEG}$ and AlTSA$_{PVA-PEG}$ samples present acid sites with similar acid strength, with $E_i = 570$ and 580 mV, respectively (Fig. 7a and b). These values are higher than those of the corresponding immobilized copper salts CuTPA$_{PVA-PEG}$ ($E_i = 540$ mV, Fig. 7a) and CuTSA$_{PVA-PEG}$ ($E_i = 450$ mV, Fig. 7b). On the other hand, all the immobilized salts present acid strength considerably higher than that of the sites present in the PVA-PEG matrix used for the immobilization ($E_i = -63$ mV).

It was determined by this technique that the immobilized aluminum salts (AlTSA$_{PVA-PEG}$ and AlTPA$_{PVA-PEG}$) present a total number of acid sites higher than that of the corresponding copper (CuTSA$_{PVA-PEG}$ and CuTPA$_{PVA-PEG}$) samples.

These sites can be Brønsted and/or Lewis type. The presence of both types of sites has been reported for the AlPW$_{12}$O$_{40}$ and Cu$_{1.5}$PW$_{12}$O$_{40}$ salts, as measured by IR spectroscopy, adsorbing pyridine or NH$_3$ as probe molecule [1]. It has also been proposed that the Brønsted type acidity, detected on neutral salts of TPA or TSA, is due to H$^+$ ions formed by dissociation of water molecules coordinated to the metallic cation, according to the following reaction:

$$[M(H_2O)_m]^{n+} \leftrightarrow [M(H_2O)_{m-1}(OH)]^{(n-1)+} + H^+$$
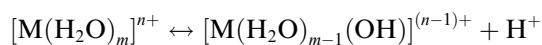
The higher amount of acid sites displayed by the polymer-immobilized aluminum salts could be explained taking into account that the Al^{3+} cations, that present absolute hardness values higher than Cu^{2+} cations [19], are more effective to form the H$^+$ ions by water dissociation.

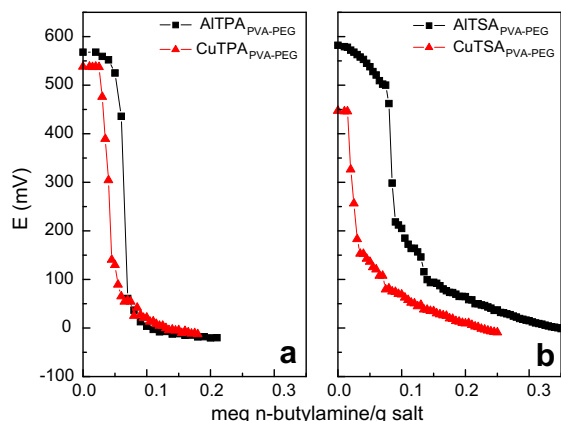On the other hand, it was confirmed the good ability of PVA-PEG blend to immobilize the tungstophosphates and tungstosilicates salts. Neither tungsten nor aluminum or copper were detected in the organic phase by atomic absorption spectrometry, showing that there was not a detectable migration of Al(Cu)TPA or Al(Cu)TSA to the organic phase when immobilized salts were refluxed in toluene or dichloromethane. Taking into account these results, and that the Al(Cu)TPA$_{PVA-PEG}$ and Al(Cu)TSA$_{PVA-PEG}$ samples present very interesting acidic properties and a good thermal stability, we can consider them as promising catalysts for many processes in replacement of conventional liquid ones.

4. Conclusions

Aluminum or copper tungstophosphates and tungstosilicates were synthesized and immobilized in a blend formed by polyvinyl alcohol and polyethylene glycol using the freeze-thawing method. The salts retained the Keggin structure of the heteropolyanions during their synthesis and immobilization.

According to the potentiometric titration measurements, the immobilized salts present very strong acid sites. The AlTSA$_{PVA-PEG}$ and AlTPA$_{PVA-PEG}$ samples display acid strength and a total number of acid sites higher than that of the corresponding copper ones.

It has been confirmed the good ability of the polymeric matrix constituted by polyethylene glycol and polyvinyl alcohol to immobilize aluminum or copper tungstophosphate and tungstosilicate salts.

This type of catalyst can be utilized in acid reactions carried out in liquid phase at relatively low temperatures, without an appreciable loss of the catalytically active species, in replacement of the homogeneous catalysts conventionally employed.

Fig. 7. Potentiometric titration curves of aluminum or copper immobilized salts from TPA (a) and TSA (b) heteropolyacids.

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